Chemistry. — *Membrane and Osmosis.* V. By F. A. H. SCHREINEMAKERS.

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Osmosis of binary liquids through a membrane $M(n)$.

In Comm. M.O. III we have discussed some phenomena, which may occur with the diffusion through a membrane $M(W)$ (positive and negative osmosis, etc.) ; we deduced them with the aid of the O.W.A. of the liquids and also with the aid of the W-amount which these liquids give to the membrane. We found among other things :

A_1. when two liquids give a different W-amount to a membrane $M(W)$, the water will diffuse from the liquid giving the greater W-amount to the membrane, towards the liquid giving the smaller W-amount to this membrane.

If we consider the W-amount of the two boundary planes of the membranes, then we can say also :

A_2. the water diffuses in a membrane $M(W)$ from the boundary plane having the greater W-amount, to the boundary plane having the smaller W-amount.

Now we shall say :

A_3. in a membrane $M(W)$ the water runs "downward" ; or : in a membrane $M(W)$ is a "down W-current".

As this result obtains not only for water, but also for every other substance, we consequently have in general :

B. in a membrane permeable for one substance only, this substance runs downward ; or : in a membrane permeable for one substance only is a downcurrent.

Instead of a membrane, permeable for one substance only, we now take a membrane $M(n)$; on one boundary plane it will get a certain amount of the substances W, X, Y etc. and on the other boundary plane a certain different amount of these substances. If we now assume that each of these substances runs downward in this membrane also, then we should have :

C_1. in a membrane $M(n)$ all substances run downward ; or : in a membrane $M(n)$ all currents are downcurrents.

It is evident that these various downcurrents need not have the same direction ; e.g. when the left side boundary plane has a greater W- but a smaller X-amount than the right side one, then the down W-current will go towards the right and the down X-current towards the left.

In Comm. M.O. III we have deduced what was said above sub B ; as we shall see later on, however, this deduction does not obtain any longer for a membrane $M(n)$. Instead of C_1 we might also assume now that one (or more) of the substances passes through the membrane in the opposite direction, viz. from the boundary plane in which this substance has the smaller W-amount towards the boundary plane in which this substance has the greater W-amount. Then we shall say: this substance runs upward, or there is an upcurrent. Instead of C_1 we should then have :

C_2. in a membrane $M(W)$ one or more of the substances can also run upward ; or also : there may be one or more upcurrents in a membrane $M(n)$.

We may summarise all that has been discussed above, also by saying :

D. when there is only one current in a membrane, this will be a down current ; when there are more currents, then there may be upcurrents also.

We shall refer to this later on.

We now consider the osmotic system :

$$L \mid M(n) \mid L' \qquad (1)$$

in which L and L' are binary liquids ; we imagine them represented by two points on line WX of figs. 1—4 ; for the sake of concentration we suppose as we did also in Comm. M. O. IV that in these figures the left side liquid L of system (1) is also situated on the left side of liquid L'. The figs. 1—4 of this communication are the same as the figs. 1—4 of Comm. M.O. I ; the fully drawn curve $W'X$ is the W-curve and the dotted curve WX' the X-curve of the membrane $M(n)$.

In Comm. M.O. IV we have seen that with the osmosis in system (1) the *D.T.'s* *a*, *b* and *c* of scheme I and the transition-*D.T.'s* *e* and *f* of scheme II can occur ; the *D.T.'s* between parentheses are not possible.

SCHEME I.

	W	X
a.	⟵ 0	⟵ (cond.)
b.	⟶	⟵
c.	⟶	⟶ 0 (cond.)
d.	[⟵ 0	⟶ 0]

SCHEME II.

	W	X
e.	——	⟵
f.	⟶	——
g.	[——	⟶ 0]
h.	[⟵ 0	——]

In Comm. M.O. IV we have deduced this with the aid of the O.W.A. and O.X.A. of the liquids ; we can also deduce this now with the aid of the W- and the X-amount which these liquids give to the boundary plane of the membrane.

We then begin by assuming that C_1 obtains viz. that W and X run downward, so that there are only downcurrents in the membrane.

We now take the osmotic system :

$$\left.\begin{array}{ccc} a_1 \mid M(n) \mid a_2 & & \text{fig. } 1 \\ \longrightarrow W \quad \longleftarrow X & & \text{D.T. } b \end{array}\right\} \qquad (2)$$

This means that we have a membrane $M(n)$, the W- and X-curves of which are represented by fig. 1 ; the two liquids a_1 and a_2 are represented by the points a_1 and a_2 of this same figure 1. The arrows indicate the directions in which the substances diffuse.

The left side liquid a_1 namely gives a greater W-amount to the membrane than the right side liquid a_2 (viz. $a_1\, w_1 > a_2\, w_2$). If we now assume that a boundary plane is approximately in equilibrium with the liquid, then the left side boundary plane will consequently get a greater W-amount than the right side one ; so the water will now run from left to right.

The liquid a_1 gives a smaller X-amount to the membrane than the liquid a_2 (viz. $a_1\, x_1 < a_2\, x_2$) ; so the substance X diffuses from a_2 towards a_1, consequently towards the left.

It appears from scheme I that the osmosis now takes place according to the congruent $D.T.b$. From this follows :

when the W- and X-curves of a membrane are represented by fig. 1, then the osmosis takes place according to the congruent $D.T.b$ of scheme I.

We now take as a special case of (2) the system :

$$\left.\begin{array}{lll} \textit{water} \mid M(n) \mid L' & & \text{fig. } 1 \\ \longrightarrow W & \longleftarrow X & \text{D.T. } b \end{array}\right\} \quad . \quad . \quad . \quad . \quad (3)$$

We now see that the water diffuses towards the liquid and the substance X from the liquid towards the water ; consequently both liquids run through the membrane congruently.

We now take the osmotic system

$$\left.\begin{array}{lll} a_1 \mid M(n) \mid a_2 & & \text{fig. } 2 \\ \longleftarrow 0\, W & \longleftarrow X & \text{D.T. } a \end{array}\right\} \quad . \quad . \quad . \quad . \quad (4)$$

in which $M(n)$ now is a membrane, of which the W- and X-curves are represented by fig. 2 ; again the arrows indicate the direction in which the substances diffuse.

It appears namely from fig. 2 that the liquid a_1 now gives a smaller W- and a smaller X-amount to the membrane than the liquid a_2 (viz. $a_1\, w_1 < a_2\, w_2$ and $a_1\, x_1 < a_2\, x_2$) ; so the water and the substance X now both diffuse from a_2 towards a_1, consequently towards the left. Now the osmosis takes place according to the mixed $D.T.$ of scheme I. The water now diffuses incongruently, as the sign o with the arrow indicates also.

We now substitute for the liquid a_2 of system (4) the liquid a_4 of fig. (2) ; we then get the osmotic system :

$$\left.\begin{array}{lll} a_1 \mid M(n) \mid a_4 & & \text{fig. } 2 \\ \longrightarrow W & \longleftarrow X & \text{D.T. } b \end{array}\right\} \quad . \quad . \quad . \quad . \quad (5)$$

The liquid a_1 namely gives a greater W-amount to the membrane than the liquid a_4 (viz. $a_1\, w_1 > a_4\, w_4$) ; the liquid a_1, however, gives a smaller

X-amount to the membrane than the liquid a_4 (viz. $a_1 x_1 < a_4 x_4$). So the substances diffuse in the direction of the arrows viz. according to the congruent *D.T.b* of scheme I.

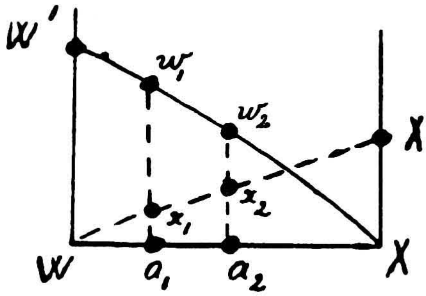

Fig. 1.

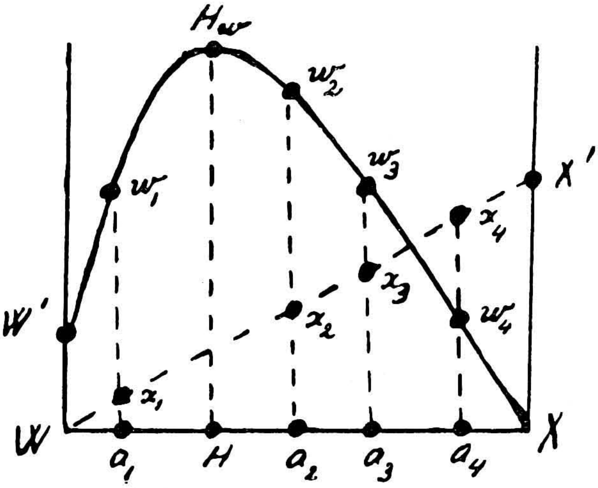

Fig. 2.

If we substitute for the liquid a_4 the liquid a_3 of fig. 2, we get the osmotic system :

$$\left.\begin{array}{lll} a_1 \mid M(n) \mid a_3 & & \text{fig. 2} \\ \longrightarrow W & \longleftarrow X & \text{D.T. } e \end{array}\right\} \quad \ldots \quad (6)$$

As the liquids a_1 and a_3 give the same W-amount to the membrane (viz. $a_1 w_1 = a_3 w_3$), no water will now consequently run through the membrane. So the substances now diffuse according to the transition *D.T.e* of scheme II.

It is easy to see now : when in fig. 2 we take two arbitrary liquids L and L', then the osmosis will always take place according to one of the *D.T.*'s *a* or *b* or according to the transition *D.T.e* ; so we may say :

when the W- and X-curves of a membrane are represented by fig. 2, then the substance X will always diffuse congruently ; the water, however, can diffuse as well congruently (*D.T.b*) as incongruently (*D.T.a*).

As a special case we now take the systems :

$$\left.\begin{array}{lll} \textit{water} \mid M(n) \mid L'(a_4 X) & & \text{fig. 2} \\ \longrightarrow W & \longleftarrow X & \text{D.T. } b \end{array}\right\} \quad \ldots \quad (7)$$

$$\left.\begin{array}{lll} \textit{water} \mid M(n) \mid L'(W a_4) & & \text{fig. 2} \\ \longleftarrow 0\, W & \longleftarrow X & \text{D.T. } a \end{array}\right\} \quad \ldots \quad (8)$$

In them L' (Wa_4) represents a liquid between the points W and a_4 and L' ($a_4 X$) a liquid between the points a_4 and X in fig. 2. If in this figure we suppose $WW' = a_4 w_4$, we find that the arrows in (7) and (8) indicate the direction in which the substances diffuse. So we find :

when the W- and X-curves of a membrane are represented by fig. 2 the water may diffuse as well from the water towards the liquid as from the liquid towards the water.

We now consider the system :

$$water \mid M(n) \mid L' \qquad \text{fig. 2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

The substance X diffusing towards the water, as is shown by (7) and (8), this now changes into an X-containing liquid. If, however, we suppose the quantity of water very large with respect to the quantity of L' or this water substituted continuously by other water, we may assume that on the left side of the membrane practically pure water is found continuously.

If we leave the system to itself now, then the liquid L', giving off X continuously, will also pass at last into a liquid, practically consisting of pure water ; so in fig. 2 the liquid L' moves towards point W.

We now imagine for L' in (9) a liquid, situated in fig. 2 between a_4 and X ; then the substances will diffuse as in system (7) ; the water will then run towards the liquid.

As soon as L' has passed the point a_4, however, and is situated, therefore, between W and a_4, the substances will diffuse as in system (8) ; then the water runs from the liquid towards the water.

From this appears :

in the beginning of the osmosis water diffuses towards the liquid ; after some time water diffuses away from the liquid towards the pure water.

Later on we shall see that these phenomena may occur, when the liquid L' consists of water and tartaric acid.

We now consider the osmotic system :

$$\left.\begin{array}{llll} & water \left| \dfrac{M_1(n)}{M_2(n)} \right| L'(Wa_4) & & \\ M_1(n) \longrightarrow W & & \longleftarrow X & \\ M_2(n) \longleftarrow 0\,W & & \longleftarrow X & \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

in which two membranes, which can function independently from one another ; we imagine the W- and X-curves of the membrane $M_1(n)$ represented by fig. 1 and those of the membrane $M_2(n)$ by fig. 2 ; the liquid L' is represented by a point between W and a_4 in fig. 2 ; the arrows indicate the directions in which the substances diffuse in this system.

We now can regulate the surfaces of both membranes at every moment in such a way that as much water runs towards the left as towards the right ; this combination of both the membranes then behaves as a membrane, permeable for X only. Later on we shall see that this is possible when the liquid L' consists of water + tartaric acid ; a combination of two membranes, one consisting of cellophane and the other of pig's bladder, can behave as a membrane, permeable for tartaric acid only.

In the osmotic system :

$$\left.\begin{array}{lll} L \mid M(n) \mid L' & & \text{fig. 3} \\ \longrightarrow W & \longleftarrow X & \text{D.T. } b \\ \longrightarrow W & \longrightarrow 0\,X & \text{D.T. } c \end{array}\right\} \quad \ldots\ldots \quad (11)$$

is a membrane, the W- and X-curves of which are represented in fig. 3. It appears from the shape of the W-curve that water must always diffuse towards the right now ; it follows from the shape of the X-curve that the substance X can run through the membrane as well towards the left as towards the right. Now the osmosis may take place either according to the congruent *D.T.b* or according to the mixed *D.T.c* or according to the transition *D.T.f*. It depends upon the compositions of the liquids L and L' which of these *D.T.'s* will occur ; when both liquids are situated between W and U, the *D.T.b* occurs ; when both liquids are situated between U and X, the *D.T.c* occurs ; when, however, L is situated between W and U and L' between U and X, then both *D.T.s* are possible.

In the osmotic system :

$$\left.\begin{array}{lll} L \mid M(n) \mid L' & & \text{fig. 4} \\ \longleftarrow 0\,W & \longleftarrow X & \text{D.T. } a \\ \longrightarrow W & \longleftarrow X & \text{D.T. } b \\ \longrightarrow W & \longrightarrow 0\,X & \text{D.T. } c \end{array}\right\} \quad \ldots\ldots \quad (12)$$

is a membrane, the W- and X-curves of which are represented by fig. 4. It is easy to find now that the osmosis may take place according to one

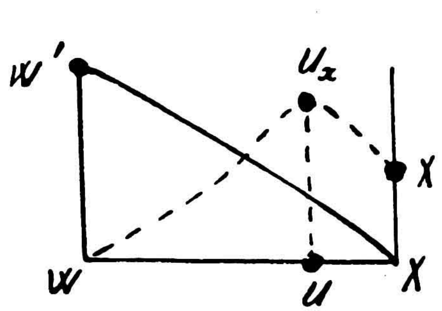

Fig. 3.

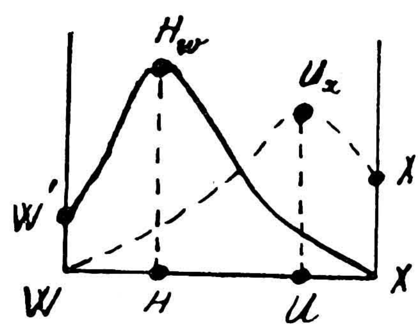

Fig. 4.

of the *D.T.'s a, b* and *c* or according to one of the transition *D.T.'s* e or *f* ; of course it depends upon the composition of the two liquids, which of these *D.T.'s* will occur.

In Comm. M. O. IV we have deduced, with the aid of the O.W.A. and O.X.A. of the liquids, that the *D.T.'s a, b* and *c* of scheme I are possible ;

in this communication we found the same with the aid of the W- and the X-amount the liquids give to the membrane. It also became clear from this that when in the membrane of a system only downcurrents occur, the $D.T.$ of a system will follow from the W- and X-amount the liquids give to the membrane, consequently from the W- and X-curves of the membrane.

If, however, we omit this restriction and if we assume, therefore, that also upcurrents may occur, then it is clear that the three $D.T.$'s a, b and c still remain possible; then, the $D.T.$ of a system, however, can no longer be deduced from the W- and X-curves of its membrane.

In order to illustrate the above, we shall first consider one more system, in which only a single substance diffuses. For this obtains what was said in A_3 or B viz.: in a membrane, permeable for one substance only is a downcurrent. In order to deduce this in a way differing a little from the one we applied before, we take the system:

$$n \times L \mid \qquad \mid n' \times L' \quad . \; . \; . \; . \; . \; . \; . \quad (13)$$

in which the liquid may contain an arbitrary number of substances; for the sake of concentration we assume that L gives a greater W-amount to the membrane than the liquid L'. The boundary planes of the membrane have been indicated by the vertical lines.

We now imagine the right side boundary plane shut off by an impermeable wall; we then represent this system by:

$$n \times L \mid \quad u \quad \| \, n' \times L' \quad . \; . \; . \; . \; . \; . \; . \quad (14)$$

in which u is the W-amount the membrane gets in the liquid L; when there are m quantities of this membrane, this will contain mu mol. of water.

If we now place the impermeable wall on the left side of the membrane, then so much water will run from the membrane towards the right till the right side liquid is in equilibrium with the membrane. As this right side liquid changes its quantity and its composition in this way, we represent the new system by:

$$n \times L \, \| \quad u'_1 \quad \mid n'_1 \times L'_1 \quad . \; . \; . \; . \; . \; . \; . \quad (15)$$

in which u'_1 is the W-amount the membrane gets in the new right side liquid L'_1. The right side liquid now has taken up $m\,(u - u'_1)$ mol. W.

We now place the impermeable wall once more on the right side of the membrane, water will now run from the liquid L towards the membrane; we then get the system:

$$n_1 \times L_1 \mid \quad u_1 \quad \| \, n'_1 \times L'_1 \quad . \; . \; . \; . \; . \; . \; . \quad (16)$$

in which u_1 is the W-amount the new left side liquid L_1 gives to the membrane. So the left side liquid has given off $m(u_1 - u'_1)$ mol. W to the membrane. We now find: with the transition of (14) into (16):

$$\text{liquid } L \text{ has given off } m\,(u_1 - u'_1) \text{ mol. } W$$
$$\text{liquid } L' \text{ has absorbed } m\,(u - u'_1) \text{ mol. } W.$$

The remainder, after subtracting these quantities viz. $m(u - u_1)$ mol. W has been given off by the membrane.

If we take m small with respect to n and n', then L, u and L' of system (14) differ only a little from L_1, u_1 and L'_1 in (16).

If we call the transition of the water, mentioned above, a "sluice current", then we may say therefore :

E_1. the sluice current takes the water from the liquid, giving the greatest W-amount to the membrane, towards the liquid, giving the smallest W-amount to this membrane.

Consequently we may say also :

E_2. the sluice current takes the water in the same direction as a membrane, in which the water runs downward.

As the sluice current is always possible, follows :

E_3. in a membrane $M(W)$ a downcurrent is always possible.

As with the diffusion of water only two directions can be imagined however, one of which is impossible, follows :

E_4. in a membrane $M(W)$ the water must run downward.

We now imagine a membrane $M(n)$ in system (14) instead of a membrane $M(W)$; this will then get a definite W-, X-, Y-amount, etc. By moving the impermeable wall we then get once more the corresponding systems (15) and (16). Instead of E_1 we now have :

F_1. the sluice current takes every substance from the liquid, giving the greater amount of this same substance to the membrane, towards the liquid giving the smaller amount of this substance to the membrane.

So it depends upon the absorption of the membrane whether this sluice current will take all substances in the same direction, or some substances towards the left and other substances towards the right.

Instead of E_2 we now have :

F_2. the sluice current takes all substances in the same direction as a membrane in which all substances run downward.

As the sluice current is always possible, it follows :

F_3. in a membrane $M(n)$ a *D.T.* is possible in which all currents are downcurrents.

Consequently a complete analogy exists as far as this between the membranes $M(W)$ and $M(n)$. If now there were only two *D.T.'s*, one of which should be impossible, then in accordance with E_4 we might conclude also : in a membrane $M(n)$ only downcurrents are possible ; as, however, more *D.T.'s* are possible (viz. the congruent one and the several mixed ones) we may not draw this conclusion. So these considerations do not raise any objection to the assumption :

F_4. in a membrane $M(n)$ upcurrents may occur as well as downcurrents.

Reversally it does not follow from this of course that upcurrents can occur in reality ; we shall refer to this later on.

(To be continued.)

Leiden, Lab. of Inorg. Chemistry.